



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

UCRL-SR-204025

# The Role of Hydrate Films in the Effectiveness of Direct CO<sub>2</sub> Injection as an Ocean Carbon Sequestration Strategy

Catherine Goyet

May 6, 2004

## Disclaimer

---

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

# **The role of hydrate films in the effectiveness of direct CO<sub>2</sub> injection as an ocean carbon sequestration strategy**

## **FINAL REPORT**

Catherine Goyet  
University of Perpignan

30 April 2004

## **BACKGROUND**

About one-third of the carbon dioxide (2 Pg C/yr of 6 Pg C/yr) we emit into the atmosphere is already being sequestered naturally by the ocean by the process of CO<sub>2</sub> gas transfer across the air-sea interface. Over twenty years ago Brewer (1978) and Chen and Millero (1979) presented the first fundamental estimates of anthropogenic CO<sub>2</sub> in the ocean based the hypothesis of CO<sub>2</sub> penetration along isopycnal surfaces and observations of total inorganic carbon (TCO<sub>2</sub>) and total alkalinity (TA). At that time the anthropogenic CO<sub>2</sub> signal was not as large as today and given the uncertainty of the approach, the uncertainties of the results were generally regarded as relatively large (Shiller, 1981; Broecker et al., 1985). However, since then, variations of this approach have been used to estimate anthropogenic CO<sub>2</sub> in many areas of the world ocean (Chen, 1982; Papaud and Poisson, 1986; Poisson and Chen, 1987; Chen, 1993; Goyet and Brewer, 1993; Tsunogai et al., 1993; Wallace, 1995; Gruber et al., 1996; Peng et al., 1998; Goyet et al., 1998; Gruber, 1998; Sabine et al., 1999). A recent modeling study (Caldeira and Duffy, 2000) using the DOCS model, confirms that penetration along isopycnal surfaces is the dominate mode of natural carbon sequestration by the ocean.

A comparison of the estimates from Chen (1993) based on the original approach (Chen and Millero, 1979), and from Gruber, (1998) and Sabine et al., (1999) based on the “improved” approach that uses transient tracers to estimate ventilation ages (Gruber et al., 1996), shows the similarity and differences in the results (Chen, 2000). The similarity is in the overall global estimate of the quantity of anthropogenic CO<sub>2</sub> present in the ocean. The main differences are in the locations of penetration and storage of anthropogenic CO<sub>2</sub> in the ocean. Results from another approach based on mixing of water masses (Goyet et al., 1999) also reveals differences in the location of anthropogenic CO<sub>2</sub> in the ocean (Coatanoan et al., 2000). In the northern Indian Ocean, the depth of anthropogenic CO<sub>2</sub> penetration is estimated significantly deeper (by ~ 300m) using the approach from Sabine et al., (1999) than using the approach from Goyet et al., (1999).

Overall, the important studies cited above demonstrate that not only the ocean continuously absorbs anthropogenic CO<sub>2</sub> gas from the atmosphere but also that today it is possible to determine with reasonable confidence the amount of anthropogenic CO<sub>2</sub> in the global ocean. The Atlantic Ocean which contains approximately  $41 \pm 6$  PgC absorbs about twice as much anthropogenic CO<sub>2</sub> as the Indian Ocean and about 1.15 times more anthropogenic CO<sub>2</sub> than the Pacific Ocean. Comparison of ocean model results with

observation-based estimates (e.g., Caldeira and Duffy, 2000, 1998) is an essential step in building confidence in the model's predictive capabilities. However, key to predicting the impact and efficacy of natural or induced carbon sequestration in the ocean, is the accurate simulation of both physical and biochemical oceanographic processes.

Marine biota plays several important roles in the global carbon cycle. Marine biota fixes carbon and channels it through the food web. This carbon can be regenerated as CO<sub>2</sub> in the surface waters, where much of it would be returned to the atmosphere; the carbon can work its way through the food web to become harvestable food, or it can find itself in the deep sea where it is remineralized to CO<sub>2</sub> and sequestered for decades to centuries. These biological processes are important in moving carbon across isopycnals. There is a need to better understand these processes and in particular to better quantify the role of dissolved and particulate organic carbon. The on-going development of new technologies such as a transmissometer for POC measurements (Bishop, 1999) and large volume filtration systems provides the means to acquire the data necessary to quantify the role of organic carbon in moving carbon across isopycnals. If direct CO<sub>2</sub> injection endangers marine biology, direct CO<sub>2</sub> injection could be counterproductive: It could produce worse environmental impacts than atmospheric CO<sub>2</sub> release, and could disrupt the natural biological carbon pump diminishing the effectiveness of direct injection as a CO<sub>2</sub> sequestration strategy. Whereas these extreme scenarios may prove unlikely, these possibilities must be examined prior to any large-scale implementation of direct CO<sub>2</sub> injection.

Today there are three main strategies considered for ocean carbon sequestration: (1) enhancement of the natural biological pump by ocean fertilization (hoping to increase the downward flux of organic carbon through increases of productivity and/or increases in biological pump efficiency), (2) artificial delivery of CO<sub>2</sub> to deep waters by direct injection (a process that avoids the biologically rich surface layer altogether), and 3) artificial delivery of CO<sub>2</sub> to the ocean by accelerated carbonate dissolution. All strategies raise issues regarding (i) environmental impacts (i.e., whether impacts on oceanic ecosystems will, in the long run, cause more significant environmental problems down the road), and (ii) feasibility and effectiveness (i.e. whether it can be done technically and whether the amounts of carbon that would be sequestered would be significant). Evaluation of these options must be made both in the context of the impacts of unchecked increase of anthropogenic CO<sub>2</sub> in absence of sequestration efforts, and relative to other sequestration options. Here, we focus only on the effects of direct injection of CO<sub>2</sub> in the ocean.

## CONCLUSIONS

The overriding objective of this research was to help society to protect our environment by reducing the amount of CO<sub>2</sub> gas in the atmosphere, thus mitigating global warming. To that end, we examined technical issues relating to the direct injection of CO<sub>2</sub> in the ocean.

Before this work began, it was thought that hydrate films on CO<sub>2</sub> droplets in the deep sea would impede droplet dissolution enough so that the droplets might rise to the surface

undissolved, degassing to the atmosphere. We now know that the droplets will dissolve within a few hundred meters of release.

This indicates that direct CO<sub>2</sub> injection into intermediate-depth waters may be effective at sequestering CO<sub>2</sub>; however, doing so may have significant adverse biological impacts and lead to higher long-term atmospheric CO<sub>2</sub> contents.

Our scientific goals have been accomplished

(a) the hypothesis has been tested showing for buoyant hydrates, the CO<sub>2</sub> bubbles will not rise until they get out of the stability field, but will dissolve within several hundred meters of release.

(b) it follows that effectiveness of CO<sub>2</sub> sequestration by direct injection at mid-depths appears to be feasible despite the formation of hydrate films.